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Interaction of Graphene ribbon with atmospheric chemical species

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Interaction of Graphene Ribbons with Atmospheric Chemical Species

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Abstract:

CO desorption from graphene ribbons is an important process in interaction of atmospheric radical with graphene. This study examines how the size of the graphene ribbon affects the chemistry of the CO desorption process by using Density Functional Theory. Two aspects of the size dependence were examined, namely the energy gap between the electronic low spin ground state and its high spin excited state and the fluctuation of the energy profiles of CO desorption reactions in the ground state. Using the previously reported 3-step mechanism, the results obtained from our calculations showed that, in the ground state, as graphene size increased, energy profiles of CO desorption reactions slightly fluctuated from that of small graphene model. However, the electronic energy gaps between the ground and some excited states of most stationary points along the reaction coordinate was strongly size dependent; particularly, such gaps could reach a thermally accessible range, i.e. smaller than 5.0 kJ/mol. Therefore, graphene chemistry, e.g., CO desorption from graphene ribbons, is more complicated than previously known due to the contribution of degenerate excited-state reaction channels in the adiabatic approximation framework; or conical or intercrossing of potential energy surfaces in non-adiabatic treatments.

Introduction

Graphenehas emerged as a new generation of carbon-based materialswith numerousprospects of applications; nevertheless,the actual number of graphene-based devices remainslimited. This is mainly because of the vanishing band gap of two dimensional (2D) graphenesheets. It has been an aim to open graphene band gap while reserving other features to make it useful material for electronic industry. An effective approach that meets these need sis to employ the quantum confinement effect. In order to control these processes, fundamental understandings about size dependence of graphenechemistry are essential.

Depending on their shapes and sizes, finite-size graphenes (e.g., PAHs) might have different electronic ground states. Previous studies consistently showed that the electronic energy gap between graphene low spin ground state andother high spin excited states decreasedwhenits size increased. Such small energy splitting is likely to affect the calculated rate constants, particularly when adiabatic electronic ground state approximation is used.

These findings could be briefly summarized as follow: i) the electronic structure of graphene clusters (e.g., spin ground states) were found varying with respect to their shape and size; and ii) in its turn, graphene chemistry was controlled by graphene electronic structures. Therefore, graphene chemistry tend to depend on its shape and size. In this study, such size dependence would be examined using the first principle quantum chemistry calculation. The CO desorption reaction would be used as a prototype.

Results and Discussion

1. CO desorption mechanism

The CO desorption from graphene edge might occur via a three-step reaction pathway, shown in Fig.1 . The first two steps involved the rearrangement of oxygen-containing functional groups at graphene active sites to form the two intermediates, a three-membered ring complex (ZN-I1) formed in the first step, and a carbonyl complex (ZN-I2) in the second step. The secondcarbonyl intermediate (ZN-I2) differs from graphene semiquinone by a carbonyl functional group locating outside the graphene lattice (>C=C=O).This intermediate facilitated the CO desorption that produced graphene desorption product. This product designated as ZN-P might be either an open-structure or a five-membered ring structure. The whole reaction pathway went through three transitionstates (TS's), namely ZN-T1, ZN-T2 and ZN-T3, respectively.

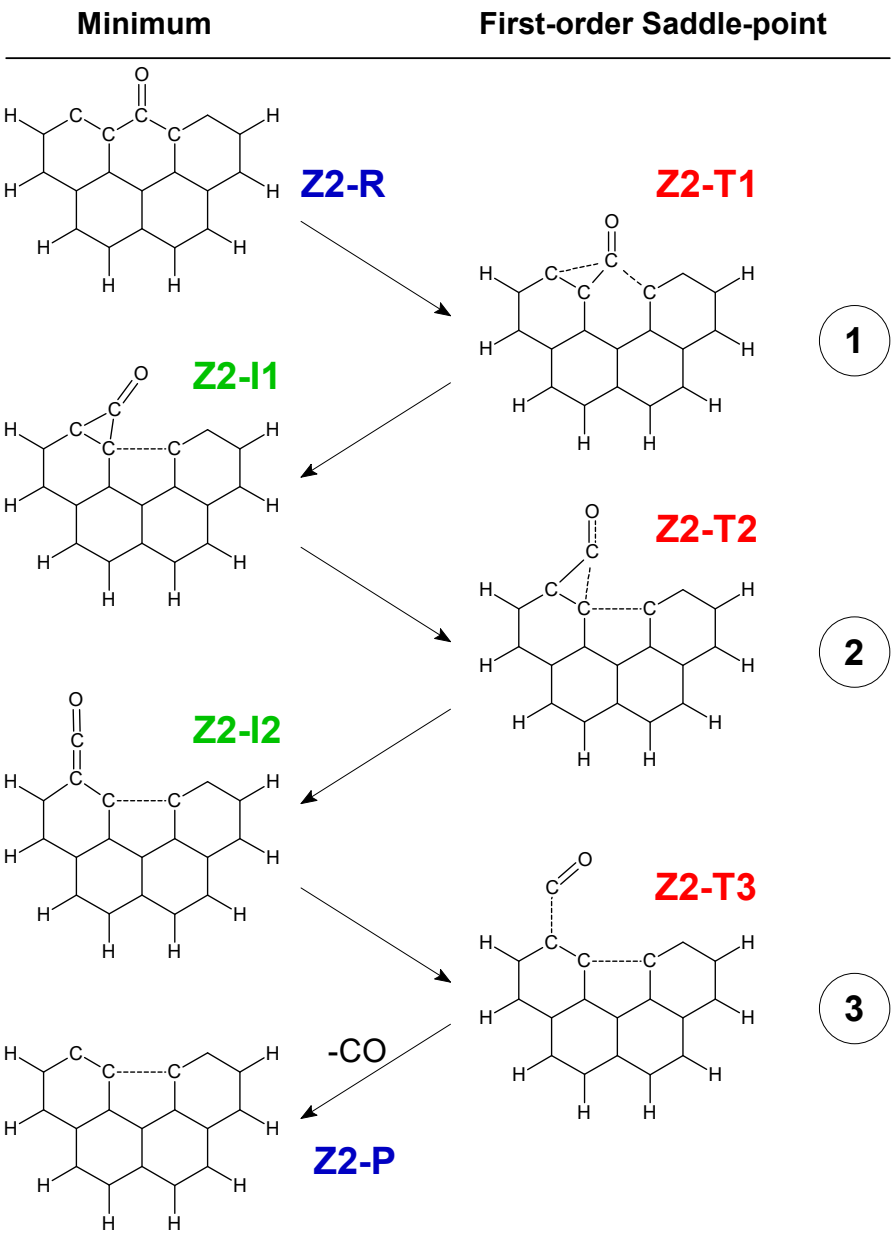

Figure 1. A CO desorption reaction pathway from graphene edge.

Calculated energy corrected by ZPE would be used to evaluate the adiabatic energy gaps between the low and high spin states (energy gap for short), activation energy and the reaction enthalpy at the absolute zero. In all models considered in this study, the doublet spin state was found to be the spin ground state of all stationary points.

2. Size dependenceof graphene chemistry in low spin ground state

Size dependence of the CO desorption on the low spin ground state surface could be evaluated using the variation of calculated activation energy and reaction enthalpy with respect to graphene size. Shown in Fig. 2 is the energy profiles along the CO desorption reaction coordinate.

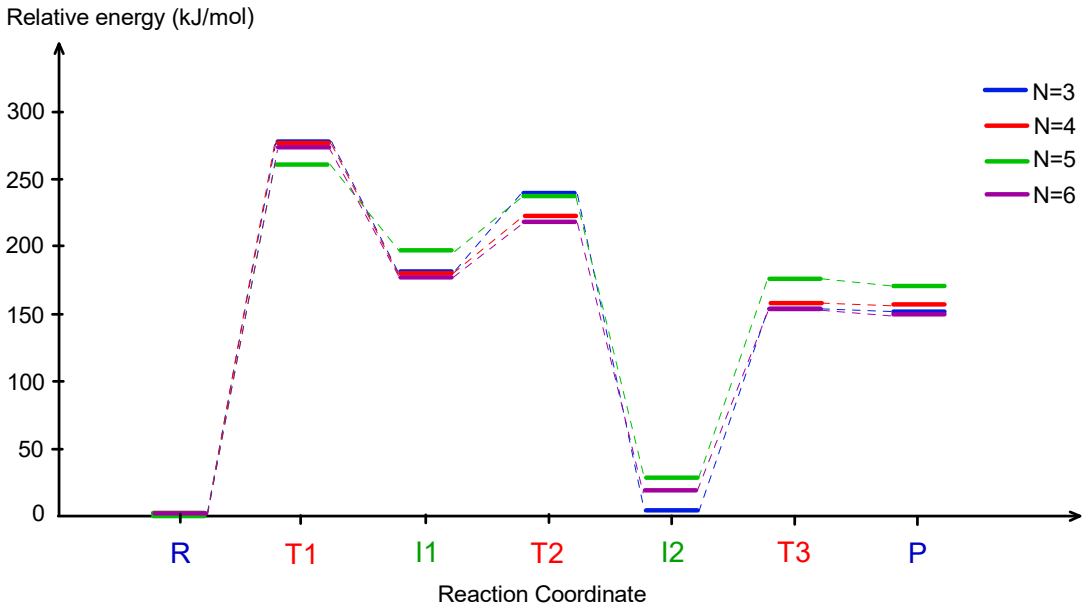

Figure 2. Energy profiles of CO desorption reaction at the doublet ground state.

It can be shown that the effects of graphene size on the reaction enthalpy and activation energy are not monotonic. For instance, the calculated activation energy of the rate limiting step (i.e., the first step) was about 277.6 kJ/mol for N=3 (the highest), and 274.2 kJ/mol when N=6. Note that the average barrier was about 272.5 kJ/mol with a standard deviation of 5.69 kJ/mol. Similarly, the reaction enthalpy was about 151.7 kcal/mol for N=3, and 149.5 kJ/mol when N=6; whereas the highest reaction enthalpy was 172.2 kJ/mol when N=5. The relative energy differences of other stationary points were also found small (e.g., within 27.8 kJ/mol) when the number of carbon atoms ranges from 30 to 54. Such small energetics variation partially proved that chosen graphene models were sufficiently physical.

3. Size dependence of graphene chemistry in high spin excited state

Size dependence of CO desorption could be investigated by examining the variation the energy gap between low and high spin state at all stationary points along the reaction coordinate. Such electronic energy gaps could be estimated as vertical or adiabatic excitation energy.

Tabulated data have showed that the absolute difference between vertical and adiabatic excitation energy was small. This unveiled the fact that ground and excited state geometry of stationary points along the reaction coordinate was very close together.

Table 1.The vertical and adiabatic excitation energies of stationary points along the CO desorption reaction coordinate, and their absolute differences. Graphene size investigated was N=6, the largest model in our current study.

Structure	Vertical Excitation Energy (kJ/mol)	Adiabatic Excitation Energy (kJ/mol)	Absolute Energy Difference (kJ/mol)
Z6-R	3.1	3.2	0.1
Z6-T1	43.4	34.7	8.7
Z6-I1	40.8	32.9	7.9
Z6-T2	42.2	34.1	8.1
Z6-I2	17.2	3.5	13.7
Z6-T3	4.2	4.5	0.3
Z6-P	3.5	4.0	0.5

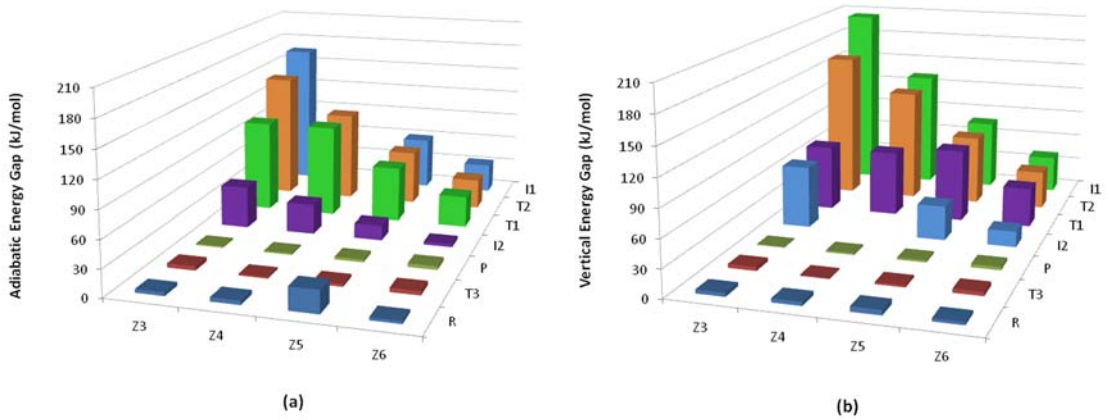

Figure 3. Plots of energy gaps (kJ/mol) between the ground and first electronic excited states with respect to graphene size (N), (a) adiabatic approximation and (b) vertical excitation. The gaps are either constantly small or size-dependently decrease to thermal accessible range.

To systematically investigate size dependence of graphene chemistry addressed in the CO desorption, full adiabatic energy profiles of the reaction at low and high spin states with sizes of N=3 and 6 were plotted in Fig. 4. The stationary points along the reaction coordinate could be classified into two groups based on the variation of their energy gap with respect to graphene size.

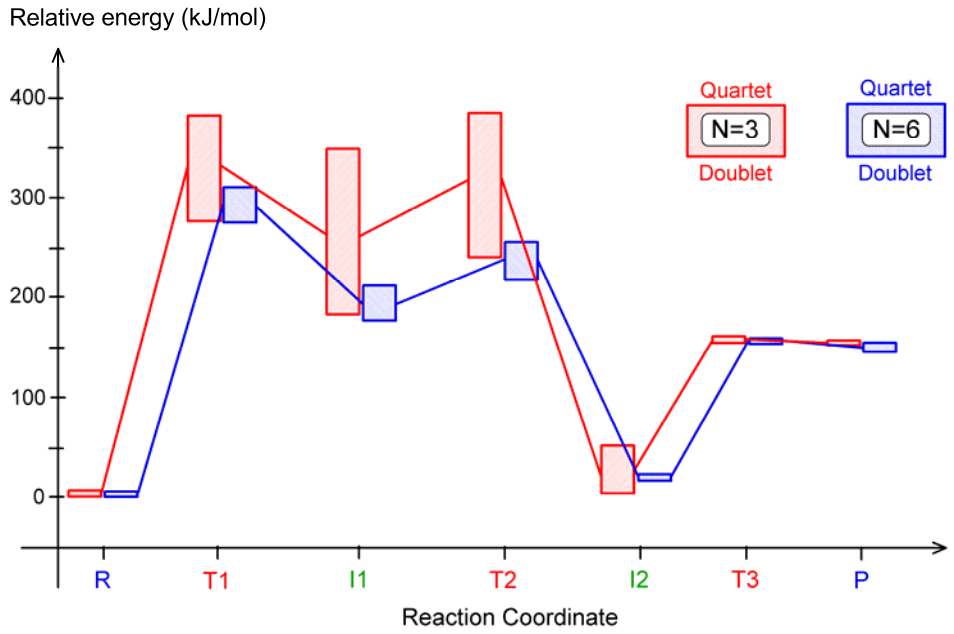

Figure 4. Energy profiles of CO desorption reaction at doublet and quartet spin states.

The first group of stationary points, consisting of thereactants (ZN-R), products (ZN-P) and the third TS complexes (ZN-T3) which always show a small energy gap regardless of graphene size.For instance, the energy gaps of reactants (ZN-R) at both sizes of N = 3 and 6 wereonly about 4.0 and 3.2 kJ/mol, respectively. These small energy gapswere consistent with CASSCF results reported using different graphene topology. Similarly, such small energy gap variations were also found for the third transition state (ZN-T3) and the graphene products (ZN-P).

The second group of stationary points, consisting of the first two transition state complexes (ZN-T1 and ZN-T2) and two intermediates (ZN-I1 and ZN-I2). The electronic energy gaps now strongly dependent on graphene size. For example, from N=3 to 6, the energy gap of the first transition state (ZN-T1)was found reduced by 69.9 kJ/mol; i.e., from 104.6 kJ/mol to 34.7 kJ/mol. Similarly, such reduction for ZN-T2 was about 109.4 kJ/mol. Therefore, the increase of graphene size by three units (N = 3 to 6) has resulted in the average decrease of energy gap of ZN-T1 and ZN-T2 by 89.7 kJ/mol. Similar results were found for the two intermediates, ZN-I1 and ZN-I2. Interestingly, the calculated energy gap in our study were comparable with our previous work for the pair of singlet-triplet state graphene model.

The size dependence of energy gaps found could be attributed to the variation of graphene structure along the reaction coordinate; particularly, to the disruption of the pi-conjugating system. For the second group of structures, i.e. the first two transition states and the two intermediates, one of the pi-bond in graphene was first disrupted to facilitate the C-C bond breaking. This step simultaneously introduced a defect to the delocalized pi-bond system causing the decoupling of degenerate electronic states. Such effect was apparent in small graphenes (e.g., N=3) when the defect concentration was remarkable. For larger models (e.g., when the number of fused-benzene rings increases), the defect concentration became negligible, the energy gap between low and high spin electronic states got shrinking to less than 5.0 kJ/mol. It is worth noting that as graphene size was developing, eventually, most energy gaps werethermally accessible (Fig. 4) in the char coal gasification, or graphene etching condition. High

temperature conditions would favor the accessibility of electronic excited state thus supported the fluctuation between ground and excited states. Such effects would be likely to affect kinetics of graphene chemistry, particularly for CO desorption since high spin states were chemically more reactive (and very much more complicated compared with graphene chemistry at their ground state).

List of Publications and Significant Collaborations that resulted from your AOARD supported project:

a) Papers published in peer-reviewed journals

[a1] Journal name:CARBON
Title: Size dependence of graphene chemistry: A computational study on CO desorption reaction
Date: 2016, 101, 16-21|DOI: 10.1016/j.carbon.2016.01.028|.
Authors: Buu Q. Pham a, Vu H. Nguyen a, Thanh N. Truong

[a2] Journal name:JOURNAL OF PHYSICAL CHEMISTRY B
Title: Performance of First-Principles based Reaction Class Transition State Theory
Date: 2016, ASAP article|DOI: **10.1021/acs.jpcb.5b09564**|.
Authors: Artur Ratkiewicz, Lam K. Huynh and Thanh N. Truong

[**a3**] **Journal name:** CHEMICAL PHYSICS LETTERS
Title: Direct *ab initio* Study of the $C_6H_6 + CH_3/C_2H_5 = C_6H_5 + CH_4/C_2H_6$ Reactions
Date: **2016,** 646, 102–109 |DOI: **10.1016/j.cplett.2015.12.063**|.
Authors: Tam V.-T. Mai, Artur Ratkiewicz, Minh v. Duong and Lam K. Huynh

b) Papers published in peer-reviewed conference proceedings

None

c) Papers published in non-peer-reviewed conference proceedings

None

d) Conference presentations without papers

None

e) Manuscripts submitted but not yet published

None

f) Provide a list any interactions with industry or with Air Force Resaerch Laboratory scientists or significant collaborations that results from this work

None

Invited talks (event name, title , date):

[1] Name: Molecular Designs for Advanced Materials: Workshop and Conference 2015

(http://www.ccl-cmu.com/scientific-program-for-molecular-designs-for-advanced-materials-workshop-and-conference/)

Title: Graphene-based Materials Design: First-Principles Approaches

Date: 24-27 November, 2015 (Chiangmai, Thailand)

Award for best paper, best poster (title, date):

None

Award of fund received related to your research efforts (name, amount, date):

[1] Name: Investigation on the Interaction of Graphene Nanoribbons with Atmospheric Species (PI: Thanh N. Truong)

Sponsor: Department of Science and Technology, Ho Chi Minh City, Vietnam

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